

Investigators and Institutions

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Abstract of Research Objectives

Detailed knowledge of the molecular spectra of ozone and other infrared-active atmospheric species is needed for accurate calculation of atmospheric heating and cooling rates in climate models. Remote sensing experiments on the Nimbus-7 satellite and the Spacelab-3 shuttle mission have shown that space-based measurements of infrared absorption or emission can be used to accurately determine the concentrations and distributions of stratospheric species on a global scale. The objective of this research task is to improve knowledge of the spectroscopic line parameters (positions, intensities, assignments, halfwidths, and pressure-induced shifts) of key atmospheric constituents through laboratory measurements.

Summary of Progress and Results

We have recorded a new series of laboratory spectra of ozone at wavelengths between 2 and 5 μm . These measurements utilized the McMath high-resolution Fourier Transform Spectrometer (FTS) at the National Solar Observatory on Kitt Peak, Arizona. Over 18 vibration-rotation bands of $^{16}\text{O}_3$ have already been identified in these spectra. Data analysis is performed primarily at Langley Research Center, and the theoretical interpretation of the results is being done in collaboration with investigators at several other institutions in the United States and France.

Results of this work to date have greatly improved line positions and relative intensities for eight fundamental vibration-rotation bands of the most abundant isotopic form of the ozone molecule ($^{16}\text{O}_3$) in the 3.3 to 3.6 μm region (previously, line positions in most of these bands were known only within $\pm 5 \text{ cm}^{-1}$). The new dataset overlaps our earlier FTS ozone spectra covering the 5-10 μm and 10-15 μm regions; this allows the scaling of line intensities in all ozone bands from 2 to 15 μm to a consistent standard. Analyses of the spectra of ozone in the 3.3 to 3.6 μm region have also resulted in new spectroscopic constants for upper vibration-rotation levels involved in "hot bands" occurring in the 10 μm and 4.8 μm regions. Over 16 "hot bands" have been analyzed in the 10 μm region alone; parameters for many of these bands have previously been unavailable. These laboratory results are now being applied in analyses of atmospheric data. Detailed studies of the broadening of O_3 absorption lines by O_2 , air, and by N_2 using spectra from the McMath FTS and the NASA Langley tunable diode laser (TDL) system are also continuing.

We have also extended our work on the measurement of nitrogen-broadened and air-broadened halfwidths for methane and two of its isotopic variants to the 3 μm region. These studies are based on FTS spectra recorded at Kitt Peak and have resulted in the accurate determination of broadening coefficients and pressure-induced shifts for a large number of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ lines. Our studies have revealed that the halfwidths and shifts of methane lines are not the same for all isotopic species. Comparison of the results in the 3 μm region with those previously obtained in the 7.5 μm region shows small differences in broadening coefficients and large differences in line shifts.

Recently we recorded FTS spectra in the 7.5 μm region of CH_4 broadened by air and by N_2 at temperatures down to -62°C using a coolable absorption cell designed and built at NASA Langley Research Center. Analysis of these spectra to obtain the temperature dependence of air- and N_2 -broadened halfwidths and shifts of CH_4 lines is in progress. All of our research results to date have been reported in the scientific literature and are being made available to public spectroscopic databases.

Journal Publications

Rinsland, C. P.; Smith, M. A. H.; Flaud, J.-M.; Camy-Peyret, C.; and Malathy Devi, V.: Line positions and intensities of the $2\nu_2$, $\nu_1+\nu_2$, and $2\nu_1$ bands of $^{16}\text{O}_3$. J. Mol. Spectrosc., **130**, 204-212 (1988).

Flaud, J.-M.; Camy-Peyret, C.; Rinsland, C. P.; Smith, M. A. H.; and Malathy Devi, V.: Line parameters for $^{16}\text{O}_3$ bands in the 7 μm region. J. Mol. Spectrosc., **134**, 106-112 (1989).

Flaud, J.-M.; Camy-Peyret, C.; N'Gom, A.; Malathy Devi, V.; Rinsland, C. P.; and Smith, M. A. H.: The ν_2 bands of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$: Line positions and intensities. J. Mol. Spectrosc., **133**, 217-223 (1989).

Rinsland, C. P.; Malathy Devi, V.; Smith, M. A. H.; and Benner, D. C.: Measurements of argon-broadened Lorentz width and pressure-induced line shift coefficients in the ν_4 band of $^{12}\text{CH}_4$. Appl. Opt., **28**, 2111-2118 (1989).

Smith, M. A. H.; Rinsland, C. P.; Malathy Devi, V.; Flaud, J.-M.; Camy-Peyret, C.; and Barbe, A.: The 3.6- μm region of ozone: Line positions and intensities. Manuscript submitted to J. Mol. Spectrosc. (1989).

Malathy Devi, V.; Benner, D. C.; Smith, M. A. H.; and Rinsland, C. P.: Measurements of air-, N_2 -, and O_2 -broadened halfwidths and pressure-induced line shifts in the ν_3 band of $^{13}\text{CH}_4$. Manuscript submitted to Appl. Opt. (1989).

A. Title of Research

Infrared Laboratory Measurements on Stratospheric Constituents

B. Investigators and Institutions

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Dr. Walter J. Lafferty (Co-Investigator)
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C. Abstract of Research Objectives

In support of the upper atmospheric measurement program involving infrared measurements from spacecraft, aircraft, and balloon flights as well as ground-based measurements, this project uses high resolution spectra to provide reliable parameters needed to measure the distribution of molecular species of particular interest for understanding the dynamics of atmospheric chemistry. The particular interest of this work is on species involved in the halogen (ClO_x) and nitrogen oxide (NO_x and HNO_x) chemistry cycles. By using techniques, software, and instrumentation developed in this laboratory in recent years, this project measures spectroscopic quantities needed to model atmospheric spectra in order to monitor the distribution of molecular species involved in the chemistry of the upper atmosphere. These data are made available to other workers in the form of molecular parameters as well as in the form of tabulated transition data calculated from the molecular parameters.

D. Summary of Progress and Results

The four low frequency fundamental bands of nitric acid (HNO_3) have been measured and analyzed for the first time. In this work both infrared and microwave measurements were combined to obtain values for the rovibrational constants that are needed to calculate the energy levels and transitions responsible for the infrared spectrum.

The moderately strong band at 1205 cm^{-1} was also measured and analyzed. It was shown to be due to the combination band $\nu_8 + \nu_9$.

These bands have been characterized for both line position and relative intensity. The band type has also been characterized. In one case an intensity anomaly was found and measured so that an effective correction term could be given to enable us to calculate a more accurate intensity for all the lines of the band.

Spectra of the two gases, SO_2 and SO_3 , which are involved in the acid rain problem, have also been the subject of some studies. Many of the weaker transitions of SO_2 in the 450 to 600 cm^{-1} region have now been identified as due to the $^{34}\text{SO}_2$ species which comprises 4.2% of a normal sample. The low frequency ν_2 and ν_4 bands of SO_3 have also been studied and a complete set of constants have been determined that allow one to calculate the appearance of those bands with confidence.

Frequency Calibration Benchmarks

This laboratory has been involved in a collaboration on frequency calibration measurements with Joe Wells at the NIST/Boulder laboratory. New measurements on a number of bands of OCS have led to new frequency calibration data for the 490 to 3000 cm^{-1} region. By means of frequency measurements, nearly all the energy levels of OCS below 3000 cm^{-1} have now been tied to the cesium frequency standard with an uncertainty of ± 9 MHz (± 0.0003 cm^{-1}) or better.

New heterodyne measurements were also made on N_2O to provide improved accuracy for the frequency values for the ν_2 band in the 520 to 660 cm^{-1} region as well as to improve our knowledge of the lower energy levels of this molecule.

To fill a gap between the N_2O and OCS calibration data, the frequencies of a number of transitions of the strong ν_3 band of CS_2 were measured. By combining data on both $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$, which are easily seen in a low pressure sample, calibration tables were prepared for the 1460 to 1550 cm^{-1} region.

A major new input for the preparation of calibration tables is the new far-infrared heterodyne measurements that have been made on the high-J transitions in the rotational spectrum of OCS. The far-infrared measurements will give greater accuracy to our evaluation of the centrifugal distortion constants in the vibrational levels below about 1900 cm^{-1} .

E. Publications Resulting from NASA-sponsored Research 1988-1989

1. "Rotational Constants of the Lowest Torsional Component (OG) of the Ground State and Lowest Torsional Component (1G) of the First Excited Torsional State of Hydrogen Peroxide," W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, and J. W. Brault, J. Mol. Spectrosc. 127, 12 (1988).
2. "High-Resolution Measurements of the ν_2 Band of HNO_3 and the ν_3 Band of trans-HONO," A. G. Maki, J. Mol. Spectrosc. 127, 104 (1988).
3. "Heterodyne and FTS Measurements on the OCS Hot Bands near 1890 cm^{-1} ," A. G. Maki, W. B. Olson, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. 130, 69 (1988).
4. "Spectroscopic Constants for the ν_9 Infrared Band of HNO_3 ," A. Goldman, J. B. Burkholder, C. J. Howard, R. Escribano, and A. G. Maki, J. Mol. Spectrosc. 131, 195 (1988).
5. "Calibration Tables Covering the 1460 to 1550 cm^{-1} Region from Heterodyne Frequency Measurements on the ν_3 Bands of $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$," J. S. Wells, M. Scheider, and A. G. Maki, J. Mol. Spectrosc. 132, 422-428 (1988).
6. "Infrared Spectrum of the ν_6 , ν_7 , and ν_8 Bands of HNO_3 ," A. G. Maki and W. B. Olson, J. Mol. Spectrosc. 133, 171-181 (1989).

7. "Heterodyne Measurements on N_2O near 1635 cm^{-1} ," M. D. Vanek, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. 134, 154-158 (1989).
8. "Heterodyne Measurements on OCS near 1372 cm^{-1} ," M. Schneider, A. G. Maki, M. D. Vanek, and J. S. Wells, J. Mol. Spectrosc. 134, 349-353 (1989).
9. "Heterodyne Frequency and Fourier Transform Spectroscopy Measurements on OCS near 1700 cm^{-1} ," J. S. Wells, M. D. Vanek, and A. G. Maki, J. Mol. Spectrosc. 135, 84-88 (1989).
10. "Infrared Spectrum of the 1205 cm^{-1} band of HNO_3 ," A. G. Maki, J. Mol. Spectrosc. 136, 105-108 (1989).

Papers in Progress

1. "Frequency Measurements of High-J Rotational Transitions of OCS and N_2O ," M. D. Vanek, D. A. Jennings, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (in press).
2. "The ν_2 and ν_4 IR bands of SO_3 ," J. Ortigoso, R. Escribano, and A. G. Maki, (submitted to J. Mol. Spectrosc.).
3. "Calibration Tables Based on Frequency Measurements," A. G. Maki and J. S. Wells, (manuscript in preparation).

A. Title of Research.

Molecular Frequency Calibration Standards and Tunable Laser Spectroscopy in Support of Upper Atmospheric Research.

B. Investigators and Institutions.

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Martin Schneider from the Institut für Angewandte Physik, der Universität Bonn, Bonn West Germany was a NIST guest researcher in the Time and Frequency Division during portions of this period.

C. Abstract of Research Objectives.

The primary objective of this research is to provide reference tables (in the 0 to 3000 cm^{-1} region) of frequencies of molecular transitions (both transitions from the ground level and relevant hot band transitions are required to provide definitive signatures) along with other information such as relative intensities and lower energy levels. These values serve as frequency or wavenumber calibration points, not only for spectroscopic studies of molecules in the upper atmosphere, but also for the community of spectroscopists at large. The first step in the generation of these tables requires accurate heterodyne frequency measurements with a system comprised of tunable diode lasers (TDLs) and associated optics, a CO_2 laser frequency synthesizer, and CO lasers which serve as transfer oscillators. A second step in the generation of the reference tables involves fitting the data and predicting values for calibration tables from the newly determined constants.

D. Summary of Progress and Results.

Work (in the form of the two steps above) has continued on both carbonyl sulfide (OCS) and nitrous oxide (N_2O). This is part of an ongoing effort to bring a broad coverage calibration atlas (based primarily on these molecules) into fruition. Currently direct heterodyne frequency measurements are possible in our lab in the regions 860-1110 cm^{-1} (CO_2 laser coverage) and 1220 to 2080 cm^{-1} (CO laser coverage). Direct measurements were made on OCS in the 1850-1914 and 1650-1727 cm^{-1} regions [1,6]. Beyond a higher density of newly calibrated lines for definite signatures, the hot band measurements permitted calculated transitions in the regions 2508-2577 and 2695-2762 cm^{-1} [1] and 2915-2964 cm^{-1} [6]. The transfer oscillator technique was also extended for the first time into the 2080 cm^{-1} region, and new frequency measurement based calibration tables for the 1975-2090 cm^{-1} region will soon be available [12]. New OCS measurements at 1372 cm^{-1} also permitted accurate calculation outside of the region of direct measurements; a 488-557 cm^{-1} table is given in [8].

Current OCS fitting procedures call for a simultaneous fitting of all heterodyne plus other data made to date in order to obtain the best possible constants. Ref. [10] gives some results of measurements of high-J rotational transitions made on OCS (and N₂O) low lying levels. Similar work has been done on N₂O; measurements at 1635 cm⁻¹ yield tables for 519-661 cm⁻¹ [7], and hot band measurements at 930 cm⁻¹ permit a table covering 2725-2840 cm⁻¹ [11]. A gap in the coverage of OCS and N₂O in the 1400 cm⁻¹ region is partially covered by CS₂ (1460-1550 cm⁻¹) [3], and potentially by SO₂ (in progress, [14]) for the 1340-1400 cm⁻¹ region. CO transitions have now been determined by frequency measurements over the range 1250-2080 cm⁻¹ [4,9,13].

E. Journal Publications for 1988 and 1989 (References).

1. Heterodyne and FTS Measurements on the OCS Hot Bands Near 1890 cm⁻¹. A. G. Maki, W. B. Olson, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. 130, 69-80 (1988).
2. Improved Rotational Constants for HF, D. A. Jennings and J. S. Wells, J. Mol. Spectrosc. 130, 267-268 (1988).
3. Calibration Tables Covering the 1460 to 1550 cm⁻¹ Region from Heterodyne Frequency Measurements on the ν_3 Bands of ¹²CS₂ and ¹³CS₂, J. S. Wells, M. Schneider, and A. G. Maki, J. Mol. Spectrosc. 132, 422-428 (1988).
4. ¹²C¹⁶O Laser Frequency Tables for the 34.2 to 62.3 THz (1139 to 2079 cm⁻¹) Region, M. Schneider, K. M. Evenson, M. D. Vanek, D. A. Jennings, J. S. Wells, A. Stahn, and W. Urban, NBS Tech Note No. 1321 (1988).
5. Current Status of Calibration Frequencies for Tunable Diode Lasers from Heterodyne Frequency Measurements, J. S. Wells, M. D. Vanek, A. G. Maki, M. Schneider, and A. Hinz, (16 p) Monitoring of Gaseous Pollutants by Tunable Diode Lasers, D. Reidel Pub. Co. (1989).
6. Heterodyne Frequency and Fourier Transform Measurements on OCS near 1700 cm⁻¹, J. S. Wells, M. D. Vanek, and A. G. Maki, J. Mol. Spectrosc. 135, 84-88 (1989).
7. Heterodyne Measurements on Nitrous Oxide near 1635 cm⁻¹, M. D. Vanek, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. 134, 154-158 (1989).
8. Heterodyne Measurements on Carbonyl Sulfide near 1372 cm⁻¹, M. Schneider, A. G. Maki, M. D. Vanek and J. S. Wells, J. Mol. Spectrosc. 134, 349-353 (1989).
9. Heterodyne Frequency Measurements of ¹²C¹⁶O Laser Transitions, M. Schneider, K. M. Evenson, M. D. Vanek, D. A. Jennings, J. S. Wells, A. Stahn, and W. Urban, J. Mol. Spectrosc. 135, 197-206 (1989).
10. Frequency Measurements of High-J Rotational Transitions of OCS and N₂O, M. D. Vanek, D. A. Jennings, J. S. Wells and A. G. Maki, J. Mol. Spectrosc. (in press).
11. Heterodyne Frequency Measurements on N₂O near 930 cm⁻¹, A. G. Maki, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. (in press).
12. Heterodyne Frequency Measurements of OCS near 2060 cm⁻¹, J. S. Wells, M. Schneider, and A. G. Maki, J. Mol. Spectrosc. (to be submitted).
13. Heterodyne Frequency Measurements of CO Laser Transitions near 4.9 μ m, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (to be submitted).
14. Heterodyne Frequency Measurements on SO₂ near 1360 cm⁻¹, M. D. Vanek, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (in progress).

A. TITLE OF RESEARCH TASK

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY
OF
MOLECULES OF ATMOSPHERIC IMPORTANCE

B. INVESTIGATORS AND INSTITUTIONS

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C. ABSTRACT OF RESEARCH OBJECTIVES

It has been demonstrated that remote sensing techniques based upon millimeter and submillimeter (mm/submm) technology can make important contributions to atmospheric science. The planning, execution, and interpretation of those experiments require a firm knowledge of the spectroscopic properties of atmospheric molecules. Our work is designed to support these atmospheric observations via contributions to the spectroscopic data base for the microwave through infrared spectral region. The work includes both the direct measurement of millimeter and submillimeter wave spectra of important atmospheric species and the calculation of synthetic spectra from these measurements. Results include line positions and linewidths in both the ground and excited vibrational states.

D. SUMMARY OF PROGRESS AND RESULTS

During this period we have carried out measurements of line positions, widths, and intensities in the millimeter, submillimeter, and far infrared spectral regions and have done theoretical calculations in support of these measurements. Species studied include HNO_3 , NO_2 , CF_2Cl_2 , HDO , HOOH , and N_2O_5 . Much of the work finished in this period is detailed in the "JOURNAL PUBLICATIONS" section below and can only be briefly summarized here. It includes a number of extensive mm/submm studies of the rotational structure of excited vibrational states. In addition to characterizing the mm/submm spectra of these excited vibrational states, it has been found that these studies also define much of the rotational structure of the infrared bands, thus making significant contributions to both the mm/submm and infrared data bases.

The N_2O_5 work (done in collaboration with B. P. Winnewisser and M. Winnewisser in Giessen, West Germany) was especially interesting. It was motivated by a need for better information at long wavelengths so that the usefulness of these spectral regions for remote sensing of N_2O_5 could be evaluated. This work included measurements of line positions, shapes, and intensities in the $25 - 350 \text{ cm}^{-1}$ region.

We have also carried out a number of studies of pressure broadening in these species. Because of the number of lines in the mm/submm, far infrared, and infrared for which the linewidths need to be known, we have placed emphasis on methods which will allow laboratory measurements on a subset of them to be used to provide reliable predictions of linewidths for many more lines. In addition, we have completed a new system designed for pressure broadening measurements in the region between 77 K and 500 K. Although this exceeds the temperature range necessary for direct atmospheric comparisons, we feel that this wide temperature capability is important for comparisons with theory so that theory and experiment can bootstrap one another to provide reliable spectroscopic information of wide applicability.

E. JOURNAL PUBLICATIONS

R. A. Booker, R. L. Crownover, F. C. De Lucia, and P. Helminger, "Millimeter and Submillimeter Wave Spectra of the ONO' Bending Mode (ν_7) in Nitric Acid," *J. Mol. Spectrosc.* **128**, 62 (1988).

T. M. Goyette, W. L. Ebenstein, F. C. De Lucia, and P. Helminger, "Pressure Broadening of the Millimeter and Submillimeter Wave Spectra of Nitric Acid by Oxygen and Nitrogen," *J. Mol. Spectrosc.* **128**, 108 (1988).

R. A. Booker, R. L. Crownover, F. C. De Lucia, and P. Helminger, "Millimeter and Submillimeter Wave Spectra of the NO' Stretching Mode (ν_6) in Nitric Acid," *J. Mol. Spectrosc.* **128**, 306 (1988).

F. C. De Lucia and S. Green, "Recent Advances in Pressure Broadening: Experiment and Theory," *J. Mol. Struct.* **190**, 435 (1988).

T. M. Goyette, W. L. Ebenstein, S. L. Shostak, F. C. De Lucia, and P. Helminger, "Pressure Broadening of NO₂, CF₂Cl₂, HDO, and HOOH by O₂ and N₂ in the Millimeter Wave Region," *J. Quant. Spectrosc. Radiat. Transfer* **40**, 129 (1988).

R. L. Crownover, R. A. Booker, F. C. De Lucia, and P. Helminger, "The Rotational Spectrum of Nitric Acid: The First Five Vibrational States," *J. Quant. Spectrosc. Radiat. Transfer* **40**, 39 (1988).

F. C. De Lucia, B. P. Winnewisser, M. Winnewisser, and G. Pawelke, "The Far-Infrared Spectrum of N₂O₅ in the Gas Phase," *J. Mol. Spectrosc.* **136**, 151 (1989).

T. M. Goyette and F. C. De Lucia, "The Millimeter and Submillimeter Wave Spectrum of the $\nu_8 + \nu_9$ State of HNO₃, submitted for publication.

T. M. Goyette, W. L. Ebenstein, S. L. Shostak, and F. C. De Lucia, "The Pressure Broadening of NO₂ in the Millimeter and Submillimeter Spectral Region," submitted for publication.

1989 NASA Research Summary

A. The Electronic Spectroscopy of HO₂ Radicals

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Starting Date: April 1989

C. Abstract

In recent preliminary experiments we have discovered an electronic absorption band of the hydroperoxyl radical in the visible spectral region. The goal of the proposed work is to complete the rotational analysis and vibronic assignment of this band and to probe nearby wavelength regions for evidence of other spectroscopic transitions that are part of this same system. Collisional relaxation studies are also being performed to verify that the OOH spectrum that we see derives from vibrationally unexcited radicals. This is significant if the observed absorption band is to be used in atmospheric monitoring.

D. Summary of Progress and Results

Last year we found that by introducing hydrogen peroxide vapor into a glass photoacoustic cell we were able to record an absorption spectrum of the transient free radical OOH. While the rotational structure of the observed band provided convincing proof that we had detected OOH, a vibronic assignment for the observed transition could not be made. Although the rotational structure was found to be describable by a room temperature Boltzmann distribution, whether or not the absorption took place from the (0,0,0) level of the ground electronic state was not absolutely clear.

In order to gather more information about the vibronic assignment of the observed transition, we are attempting to extend our spectral measurements to longer wavelengths. This is being pursued in two ways. First, since an excimer laser pumped dye laser is much easier to use in the near-infrared than is a CW ring laser, we are extending our photoacoustic technique to the pulsed laser domain. We have very recently recorded a spectrum of the highly forbidden $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ electronic transition of O₂ using the new approach. Second, we are planning to arrange to borrow an Argon ion laser pumped titanium sapphire laser from the Spectra Physics Corporation for a few days. We should be able to quickly reproduce the ring dye laser experiments and then obtain preliminary data at longer wavelengths. Unfortunately, these commercial lasers are in high demand and we will only have a few days to work with it.

As these experiments progress, we are continuing to work on our rotational structural analysis in order to obtain optimized rotational constants for the one complete spectral band that we have already observed. A simplex optimization code has been written to accomplish this and about 40 lines have thus far been definitely assigned.

Collisional Lineshapes and Molecular Beam Spectroscopy
of Atmospheric Molecules

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Objectives:

The purposes of this program are to study collisional lineshapes and to obtain molecular beam spectra of various atmospheric molecules of interest to the NASA UARS (Upper Atmosphere Research Satellite), ATMOS (Atmospheric Trace Molecule Spectroscopy) and HALOE (Halogen Occultation Experiment) projects. The pressure broadenings, shifts and line profiles are required for quantitative monitoring of the distribution of contaminant gases and for temperature sounding of the atmosphere. Many of the molecular species of interest exhibit marked deviations in lineshape from the simple Lorentzian or Voigt profiles usually employed to model the spectral absorptions. A number of physical phenomena contribute to these lineshape distortions including collisional (Dicke) narrowing, speed-dependent collisional cross sections, non-impact (finite collision time) behavior, and collisional interferences (line coupling or line mixing). The precise measurement of these line profiles requires very high resolution infrared instrumentation such as the tunable difference-frequency-laser system and the color-center-laser photoacoustic spectrometer at NIST. Some of the heavier atmospheric molecules exhibit extremely dense, often strongly perturbed, spectra at normal atmospheric temperatures which have not been analyzed even with Doppler-limited resolution. In these cases molecular beam techniques can provide initial assignments due to sub-Doppler resolution and the considerable spectral simplification from the very low effective temperatures in an adiabatic expansion.

Summary of Progress:

Collisional Lineshapes:

Q-Branch Line Mixing: We have recorded the 2798 cm^{-1} band Q branch of N_2O and three Q-branches in the C-H stretch-bend combination region of HCCH using transmission spectroscopy with a difference-frequency laser system. The spectral profiles were examined from the Doppler limit at low pressures to the heavily overlapped regime at pressures approaching one atmosphere. The contours of these Q branches exhibit non-additive behavior in that they cannot be fit with a direct superposition of Lorentzian lines with the known intensities and positions of the components. Superposition deviations in the absorption constants are most evident near the band head and wings where most temperature sounding and monitoring is performed. These deviations arise from collisional line coupling when collisions can transfer intensity between overlapping lines in the spectra. Inelastic collisions that transfer population to states not involved in the overlapped transitions lead to normal

superposable broadening. Since the Q branches in linear molecules access only one vibrational "parity" (f level) component of doublet Π levels, we find that $f \leftrightarrow f$ conserving collisions result in line mixing while $f \leftrightarrow e$ contribute only broadening. Additional restrictions on the off-diagonal relaxation matrix elements have been imposed empirically to reduce the amount of line coupling observed, particularly for HCCH, which will require further theoretical justification and experimental verification.

Photoacoustic Measurement of Differential Broadening of the Λ Doublets of NO: In prior studies of the self and N_2 broadening of the overtone band of NO, we observed a small collision-induced asymmetry of the Λ doublets which exhibit equal widths and intensities under low-pressure Doppler-limited conditions. We have improved the precision and reliability of these measurements by using photoacoustic spectroscopy with a linear-scan-controlled color-center laser, which minimizes baseline channeling errors compared to the previous transmission spectra. The differential broadening has been observed in an Ar buffer gas to eliminate complications from rotational, vibrational and electronic resonances. The asymmetry is roughly proportional to J, reaching about 6% for $J=15.5$, and is seen in the P and R branches but not the Q branch. The anisotropy of the unpaired electron's Π orbital wavefunction in and out of the plane of rotation (Hund's case (b) admixture) appears to be responsible.

Molecular Beam Spectroscopy:

Molecular-Beam Spectroscopy of CHF_3 : The ν_1 C-H stretching fundamental band of fluoroform, CHF_3 (Freon 23), is strongly perturbed and its T=295 and 87 K Doppler-limited spectra, which we have previously recorded, have resisted analysis. We then recorded a subDoppler, T \approx 4 K spectrum using an optothermal (bolometer-detected molecules) molecular beam apparatus excited by a color-center laser. This has enabled us to assign the spectrum and identify the principal perturbations as anharmonic and Coriolis interactions with the A_1 and A_2 components of the bending combination, $\nu_4 + \nu_5 + \nu_6$. The global Fermi resonance with the C-H bending overtone, $2\nu_4$, is also under investigation.

Publications:

1. Q-Branch Line Mixing in N_2O : Effects of ℓ -type Doubling.
L.L. Strow and A.S. Pine, J. Chem. Phys. 89, 1427 (1988).
2. Doppler-Limited Spectra of the C-H Bending Overtone of Fluoroform.
A.S. Pine and J.M. Pliva, J. Mol. Spectrosc, 130, 431 (1988).
3. Molecular Beam Spectrum of the Highly Perturbed C-H Stretching Region of Fluoroform.
A.S. Pine, G.T. Fraser and J.M. Pliva, J. Chem. Phys. 89, 27270 (1988).
4. Photoacoustic Measurement of Differential Broadening of the Λ Doublets in $NO(X^2\Pi_{1/2}, v=2-0)$ by Ar.
A.S. Pine, J. Chem. Phys. 91, xxxx (1989).